concentrated in the early fractions and diphenylcyclopropylmethane (**13**) in the later ones. On the other hand, **B** and **15** were rather evenly distributed throughout the series. The ratio of these was also rather constant: 1.2 ± 0.2 for the middle fractions. From this, it was concluded that of the original 28% of **B** only 10% x 1.2 = 12% was eluted with the hydrocarbon products. Either the rest is appreciably more polar material, or **S5** was present in substantial amount and underwent ether cleavage on the column.

Evidence that the latter alternative is correct was provided by analysis of subsequent fractions. Fractions 70 to 80 (50 and 100% diethyl ether) contained appreciable amounts of material. The ^{1}H NMR spectrum of fraction 75 in CCl_4 solution showed the highly distinctive resonances of diphenylcyclopropylcarbinol; the high-field doublet of cyclopropyl methylene protons, split by 6.9 Hz, the singlet hydroxyl proton resonance at δ 1.85; the down-field half of the perturbed quartet due to the cyclopropyl methine proton with the up-field half overlapped by broad resonances between δ 0.7 and 2.46, and the complex of aromatic resonances. The vpc trace of the CCl_4 solution of this fraction gave a single peak with a retention time the same as an authentic sample. Fractions 72-79 were combined with a known weight of 1-phenylnaphthalene and analyzed by vpc. The relative peak areas when corrected for the relative sensitivities of the two materials, determined for authentic materials, indicated that the combined fractions contained 11% of diphenylcyclopropylcarbinol based on peroxyester. A lesser amount of product was also concentrated around fraction 66. The ^{1}H NMR spectrum of that fraction in CCl_4 indicates it to be the ring-opened ether, *tert*-butyl 4,4-diphenyl-3-butenyl ether (**S2**). The yield of **S2** was perhaps 3%, but it is not known whether this product is a primary reaction product or is formed, like diphenylcyclopropylcarbinol, from the ring-closed ether **S5**, either during the thermal decomposition or on the chromatographic column. These observations and the results of other "larger-scale" reactions show that **S5** is a component of **B.**

Kinetic Study of the Induced Decomposition of *tert*-Butyl 5,5-Diphenylperoxy-4-pentenoate (12) in the Presence of Triethyltin Hydride. Qualitative studies were made of the kinetics of the induced decomposition of **12** in the presence of

triethyltin hydride that leads to the formation of triethyltin 5,5-diphenyl-4-pentenoate (**S1**). Tin ester formation could be monitored by the carbonyl absorption at 1651 cm^{-1}, which was determined to obey Beer's Law in *n*-octane within a few percent. The 8-mm reaction tubes were carefully cleaned, rinsed well with distilled water and then with acetone, and finally dried at 135 °C for several hours. In a typical run, 14.6 mg of **12** (mp 42.5-43.5 °C), 20.9 g of *n*-octane and 2.947 g of triethyltin hydride were mixed and 1 mL aliquots were transferred to each of ten reaction tubes that had been constricted at the top for easy sealing. The tubes were quickly attached to a vacuum system by lengths of Tygon tubing, cooled with liquid nitrogen, degassed by three freeze-thaw cycles and sealed. The tubes were kept at -80 °C until used (within 48 h). Assuming 12% volume expansion per 100 °C temperature rise, the calculated initial concentrations at 110 °C (refluxing toluene) were 0.41 M for triethyltin hydride and 1.7 x 10^{-3} M for peroxyester **12**. Time zero was taken after a 15-30 s warm-up period, at which a first tube was removed and quenched in Dry Ice-acetone. Subsequent tubes were held at -80 °C until infrared analysis was undertaken at 1651 cm^{-1}, usually in duplicate. The absorbance-time data was fitted in each case to Eq. S21:

$$A(t) = A_\infty - (A_\infty - A_0) \exp(-k_T t) \qquad \text{(S21)}$$

using a generalized least-squares formalism,[60] where A_0, A_∞, and k_T were treated as adjustable parameters. The results obtained were: 0.002 M **12**, 0.0097 M Et_3SnH, A_∞ = 0.0387 ± 0.0008, A_0 = -0.0006 ± 0.0012, k_T (M^{-1}) = 0.0130 ± 0.0010 and rms = 0.0016; 0.00175 M **12**, 0.0444 M Et_3SnH, A_∞ = 0.0331 ± 0.0008, A_0 = 0.0012 ± 0.0053, k_T (M^{-1}) = 0.0150 ± 0.0011 and rms = 0.0011; 0.0017 M **12**, 0.41 M Et_3SnH, A_∞ = 0.0254 ± 0.0009, A_0 = 0.0023 ± 0.0012, k_T (M^{-1}) = 0.128 ± 0.017 and rms = 0.0018; 0.0018 M[61] **12**, 0.67 M Et_3SnH, A_∞ = 0.0327 ± 0.0009, A_0 = 0.0011 ± 0.0017, k_T (M^{-1}) = 0.138 ± 0.015 and rms = 0.0013. Thus, **12** decomposes approximately 10 times faster at 110 °C in 0.41 M than in 0.01 M triethyltin hydride. Further details and an analysis of the reliability of the rate data may be found in the original study.[62] Translation of the A_∞ values into yields of the tin ester suffers from uncertainties in the A_∞, in the preparation of and absorbance measurements on standard solutions, and in the determination of the initial quantity of peroxyester taken, always approximately 15 mg, so that the

yields of ~50% listed in Table S10 are probably good to no better than 10-15% (relative). The amount of triethyltin hydride consumed in the induced decompositions is expected to be 1-2 times the initial peroxyester concentration. This was checked in the first run listed above, where the initial ratio of the room-temperature concentrations of triethyltin hydride (0.0107 M) and peroxyester (0.0022 M) was the smallest. Here, the tin hydride concentration after 550 min (~10 half lives) was found to be 0.0088 M, or 0.0019 less than the initial concentration. This result gives at least partial assurance against the general incursion of additional mechanistic steps that might result in wholesale decomposition of the triethyltin hydride.

Kinetics of Decomposition of *tert*-Butyl Diphenylcyclopropylperoxyacetate (11) in Cumene. A solution of ~ 0.1 M peroxyester in cumene was allowed to stand exposed to the air at 23 °C in a thermostatted room. Disappearance of the peroxyester was monitored by recording the infrared spectra of aliquots between 1850 and 1700 cm^{-1} starting at an arbitrary time zero (about 5 min after preparation of the solution), then after 20, 40, and 270 min and 18 h. The absorbance readings at the carbonyl maximum of the peroxyester were measured with respect to a valley at 1790 cm^{-1} that appeared between the carbonyl band and a small peak at 1800 cm^{-1}. The data were fitted to Eq. S21 by a least-squares formalism[60] where A_0, A_∞, and k_T were treated as adjustable parameters. The derived value of k_T was $7.5 \pm 0.6 \times 10^{-3}$ M^{-1} s^{-1}.

Air-Induced Decomposition of *tert*-Butyl 5,5-Diphenylperoxy-4-pentenoate (12) in the Presence of Triethyltin Hydride. An attempt was made to determine the rate of air-induced decomposition at room temperature of 0.08 M **12** with 1 M triethyltin hydride as the hydrogen donor in *n*-octane by monitoring the carbonyl absorption of the peroxyester at ca. 1780 cm^{-1} in the presence of the strong, broad Sn-H stretching band of the tin hydride at 1813 cm^{-1}. Approximately 10 min after the preparation of the solution, there was a barely distinct carbonyl absorption on one slope of the large tin hydride band. Three hours later, the carbonyl band was only a shoulder on the tin hydride band and, after 6 h, no trace of the carbonyl band could now be discerned. However, a new absorption band appeared at approximately 1651 cm^{-1}, corresponding

to the carbonyl of triethyltin 5,5-diphenylperoxy-4-pentenoate **S1** and indicating a yield on the order of 90% in 6 h. When the reaction mixture was cooled in an ice bath, white tufts separated that were collected and crystallized from *n*-hexane to afford **S1** (40%), mp 121-123 °C, no depression on admixture with authentic material and confirmed by infrared and NMR spectra. In contrast, the infrared of a degassed sample after 3 h at room temperature gave at most 5% of tin ester.

Subsequent estimations of the rates of the air-induced process were made in *n*-octane solutions open to the air with different concentrations of peroxyester **12** and triethyltin hydride at room temperature by monitoring the 1651 cm^{-1} absorption. The yield of tin ester formed for different concentrations and times were: 0.002 M[63] **12**, 0.72 M Et_3SnH, 4 h, 63%; 0.00185 M **12**, 0.44 M Et_3SnH, 12 h, 75%, 18 h, 93%, and 36 h, 90%; 0.00195 M **12** 0.048 M Et_3SnH, 14 h, 6%, 20 h, 9%, and 74 h, 90%; 0.0022 M **12**, 0.0107 M Et_3SnH, 5 days stoppered, 21%, then stoppered for an additional day, 30%, exposed to air for one day, 92%, and then for a second day, 91%. Several difficulties, including evaporation of the solvent, decomposition of the tin hydride (as indicated by deposition of a white solid) over prolonged periods and nonstandard conditions for equilibration of oxygen between the air and the organic solution, make the above observations at best only semiquantitative. However, it appears that the process is air-induced, that reaction between the air and the tin hydride at least in part generates free radicals, and there is an inhibition period, perhaps representing the consumption of inhibitors or the buildup of intermediates involved in the air oxidation. The yields of tin ester may generally be in the range of 85-95%. The results indicate that attack of triethyltin hydride on the peroxy-ester O-O bond to give the tin ester **S1** is likely to have a lower activation energy process than that for the alternative attack that gives triethyltin *tert*-butyl ether plus the acyloxy-radical precursor to ring-opened radical **2**.

Viscosities of several liquids and binary mixtures were determined in a constant temperature bath at 20 °C using a modified Ostwald viscometer. Flow times for 10-mL quantities of cyclohexane (η = 0.960 cp) and benzene (η = 0.648 cp) were employed to determine the cell constants.[64] Ten measurements of the flow time made on each solution were reproducible to three

or four parts per thousand. The viscosity of freshly distilled 1,4-cyclohexadiene was found to be 0.595 cp. For mixtures of 1,4-cyclohexadiene and cyclohexane in the proportions (v/v) of 1:7, 1:3 and 1:1 gave viscosities of 0.845, 0.778, and 0.679 cp, respectively. Freshly distilled indene showed a viscosity of 1.76 cp. Viscosities of 0.28, 0.50 and 0.63 cp were found respectively for diethyl ether (lit.[65] 0.233 cp at 20 °C), tetrahydrofuran, and tetraethyltin.

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(19) This figure is correct, but the calculation on page 277 of ref. 1 should read: -13.35 + 1.00 - (-0.77) = 11.6 kcal/mol; the sign of the second term on the left term was inadvertently mistyped in the original.

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(21) Actually, this identification requires the assumption that the gas-phase combination and disproportionation reactions of ethyl radicals require no activation energy. While the experimental determination of this activation energy yielded a value of 2 ± 1 kcal/mol [Shepp, A.; Kutschke, O. *J. Chem. Phys.*, **1957**, *26*, 1020-1028], the reports that combinations of methyl radicals [Shepp, A. *J. Chem. Phys.*, **1956**, *24*, 939-943], isopropyl radicals [Metcalfe, E. L.; Trotman-Dickinson, A. F. *J. Chem. Soc.* **1962**, 4620-4628], and *tert*-butyl radicals [Metcalfe, E. L. *J. Chem. Soc.*, **1963**, 3560-3567] require no activation energy suggest that this value is likely to be in error.

(22) Halgren[1], p. 277.

(23) While transfer to the liquid phase, in the absence of polar factors, is not expected to strongly affect the activation energy, many lines of evidence available when this work was done suggested that pre-exponential factors for nonpolar processes may be expected to increase by factors of perhaps 3 to 50. See, for example: Benson, S. W. *The Foundations of Chemical Kinetics*, McGraw Hill, New York, N.Y., 1960, pp. 504-509; North, A. M., *The Collision Theory of Chemical Reactions in Liquids,* Methuen and Co., 1964, pp. 102-103; Mayo, F. R. *J. Am. Chem. Soc.* **1967**, *89*, 2654-2661; Laidler, K. J. *Chemical Kinetics*, McGraw Hill, New York, N.Y., 1965, p. 201.

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(28) Reference 27 actually reported a rate constant of 4.8×10^6 M^{-1} s^{-1} for the abstraction by the 2,2-dimethyl-3-butenyl radical. The value listed here uses the Arrhenius function for the rearrangement of the 2,2-dimethyl-3-butenyl radical subsequently redetermined by Newcomb, M.; Glenn, A. G.; Williams, W. G. *J. Org. Chem.* **1989**, *54*, 2675-2681: $\log (k/s^{-1}) = 11.00 - 5.88/\theta$.

(29) A key assumption, reached from considerations of product yield and material balance and supported by the results of a detailed mechanistic treatment, is that ~35% of radicals **3** give product hydrocarbon **15** via disproportionation reactions in which **3** loses a hydrogen atom, while the remainder participate in recombination reactions or in disproportionations in which **3** gains a hydrogen atom.[13,17] This assumption may not be quantitatively accurate, but it is difficult to see how any error made here could account for a major part of the discrepancy.

(30) Halgren[1], pp. 121-122.

(31) Halgren[1], pp. 77-78, 129-130, 281-282

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(37) Halgren[1], pp. 116-118, 273-275.

(38) Halgren[1], pp. 76-77.

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(40) Halgren[1], p. 134.

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(60) Halgren[1], pp. 208-220.

(61) Halgren[1] lists this concentration as 0.018 M, or 10 times larger, but the absorbance data presented (p. 405) are consistent with the concentration being as given here, as is the listed A_∞ value of 0.0327; a "0" apparently was omitted.

(62) Halgren[1], pp. 152-195.

(63) Halgren[1] lists this concentration as 0.02 M, or 10 times larger, but the absorbance data presented for thermolysis of this material at 110 °C (p. 158) are consistent with the concentration being as given here; a "0" apparently was omitted in recording the concentration.

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